SIMULATION METHODS FOR CHEMICALLY SPECIFIC MODELING AND PREDICTION OF THE STRUCTURE AND PROPERTIES OF ELECTROCHEMICAL INTERFACES

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OUTLINE

SCALES AND METHODS

CAPACITANCE:

    STRUCTURE AND DC RESPONSE

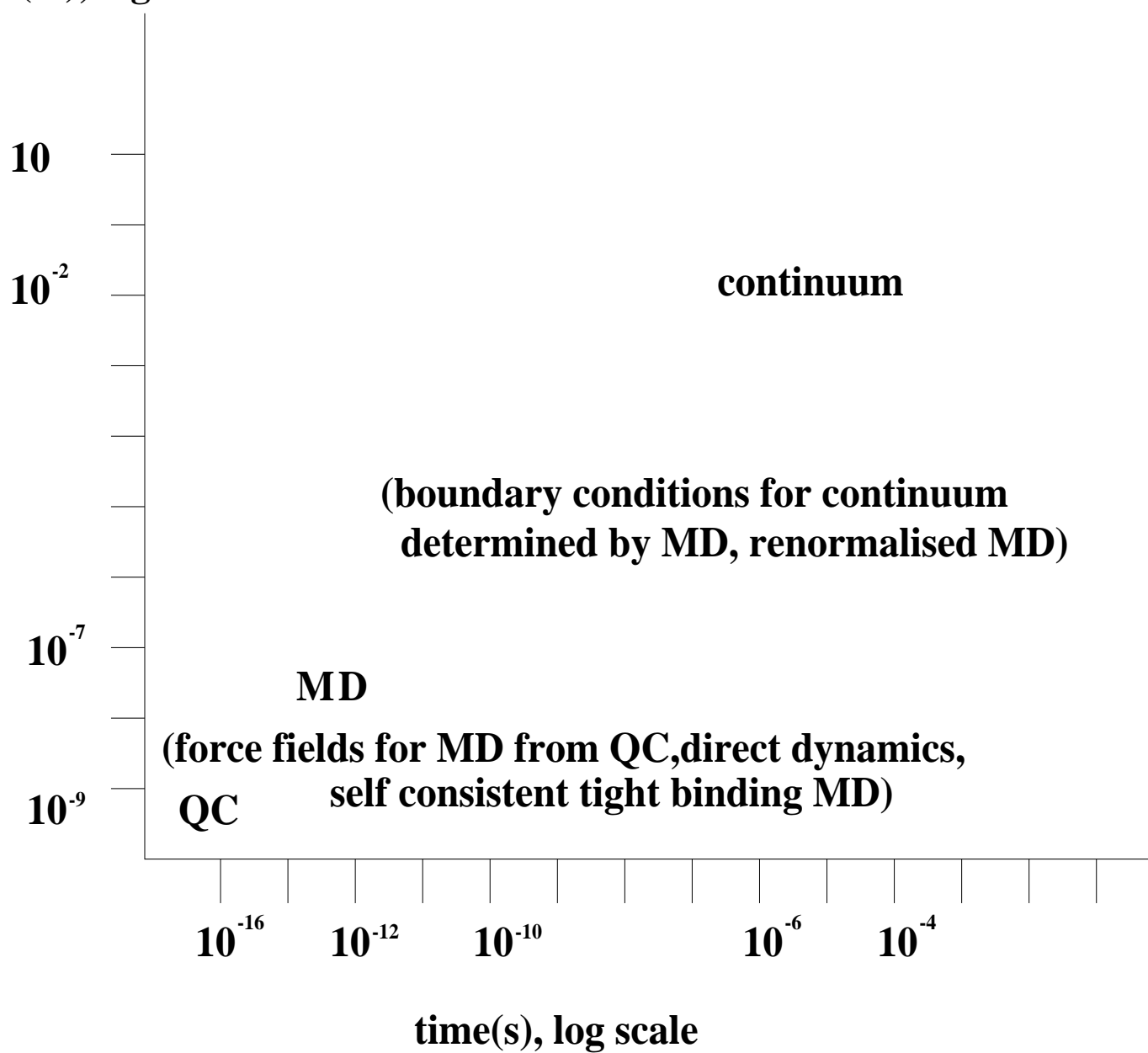ELECTRON TRANSFER:

    OUTER SHELL KINETICS

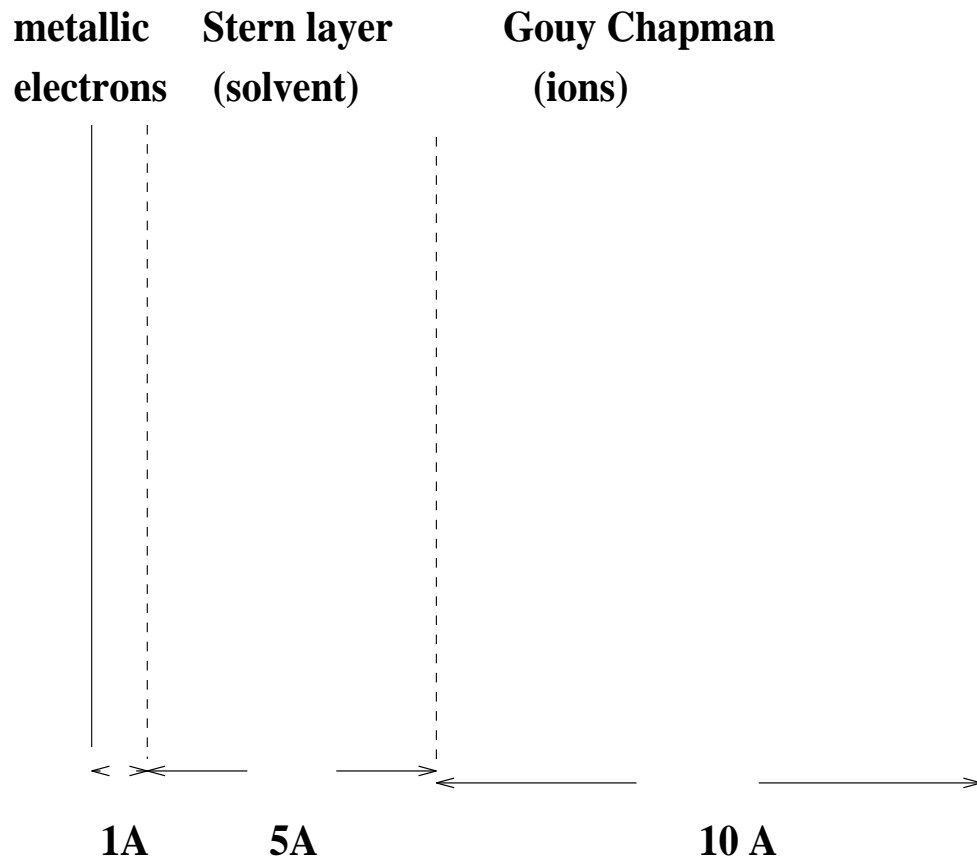SOME NEW METHODS

CONCLUSIONS AND OUTLOOK

SCALES

Diffusive	$\sqrt{D\omega}$	Reaction Diffusion	centimeters
Ion screening	$\sqrt{k_B T/4\pi e^2 \rho}$	Poisson/ Boltzman	nanometers
Dielectric		molecular dynamics	angstroms
electronic	Thomas/ Fermi	LDA, etc	0.1 angstroms

COMPUTATIONAL SCALES

distance (m), log scale

10

10^{-2} **continuum**

(boundary conditions for continuum
    determined by MD, renormalised MD)

10^{-7}

MD

(force fields for MD from QC,direct dynamics,
    self consistent tight binding MD)

10^{-9} **QC**

10^{-16} 10^{-12} 10^{-10} 10^{-6} 10^{-4}

time(s), log scale

4

metallic   **Stern layer**   **Gouy Chapman**

electrons   **(solvent)**   **(ions)**

1A   **5A**   **10 A**

$$1/C_{total} \quad = \quad 1/C_{metal} + 1/C_{Stern} \quad + \quad 1/C_{GouyChapman}$$

MODELING CAPACITANCE OF THE INTERFACE. HISTORY

- The Gouy-Chapman theory attributed the capacitance to the screening of the field by the ions of the electrolyte.

- This gives a capacitance parabolic in the charge which is observed close to the point of zero charge.

- Far from the PZC there are deviations from the theory in the experiments. These were attributed by Stern and others to the layer of water 'bound' at the interface. In most models this gives a capacitance symmetric in the charge about the PZC.

- But there is a part of the capacitance which is not symmetrical in the charge. (Grahame, 1947)

PHYSICAL PICTURE

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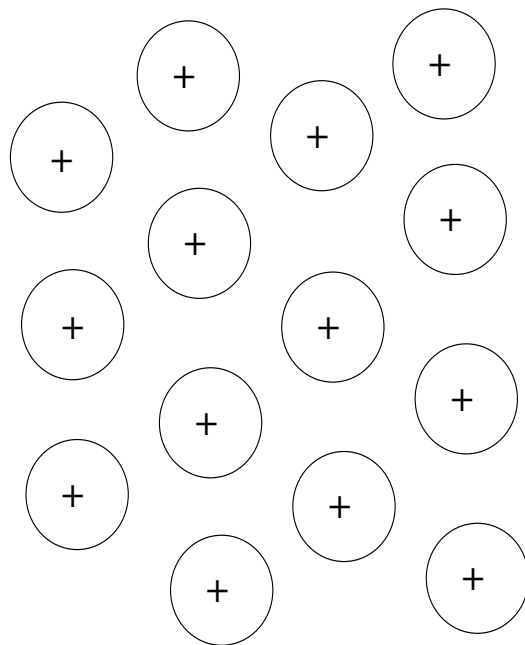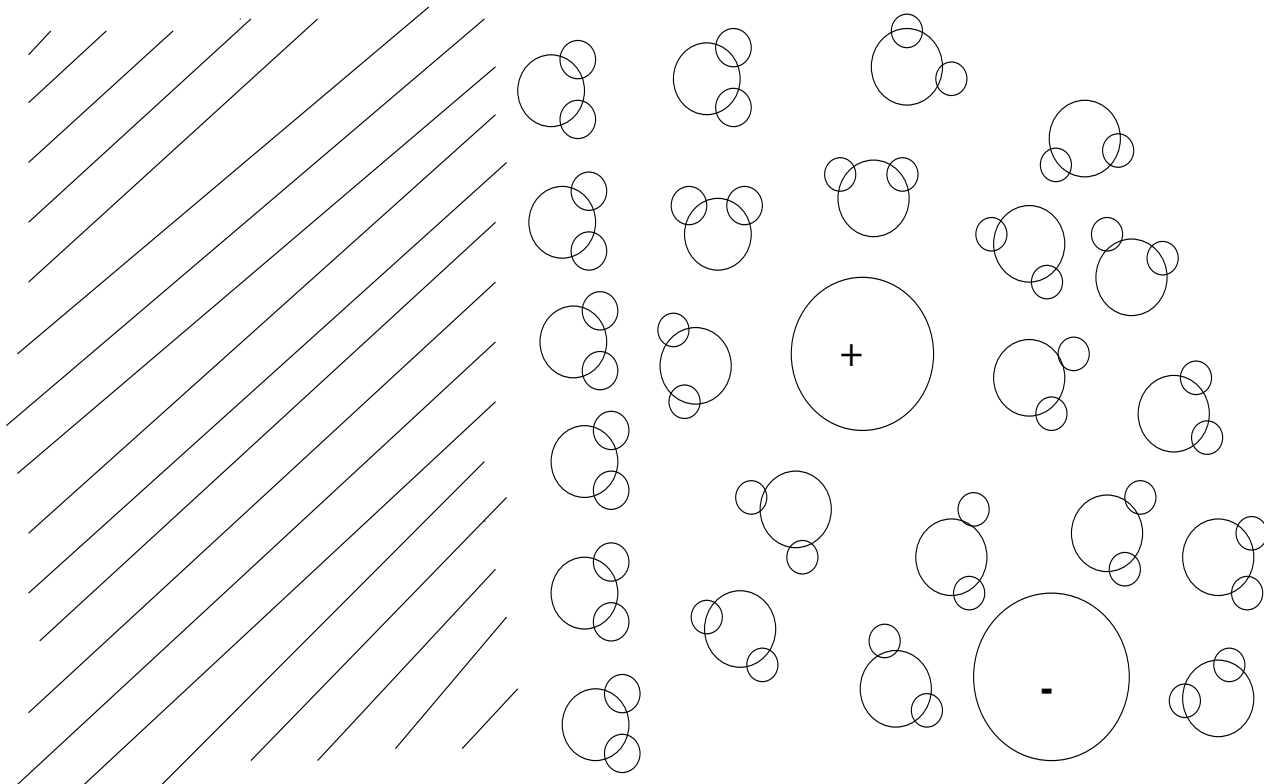
MODELLING CAPACITANCE: METAL-WATER SIDE

- A common approach, is to calculate a force field potential for a single water molecule near a metal electrode (in some model) and then fit a water-metal force field potential to the results. For example Heinzinger and coworkers as well as others used this approach for describing platinum water interfaces.

- Here we describe a Car–Parrinello type calculation combining molecular dynamics and density functional methods (J. Chem. Phys. 102, 6603 (1995);J. Chem. Phys. 109, 8076 (1998)).

- The exposed faces of the slabs are (001) or (110) surfaces of the FCC structure, with with a total of between 100 and 200 metal atoms per unit cell. (For the 100 surface the cell dimensions were 42.3Å $\times$ 15.3Å $\times$ 15.3 The 100 cell is shown below.

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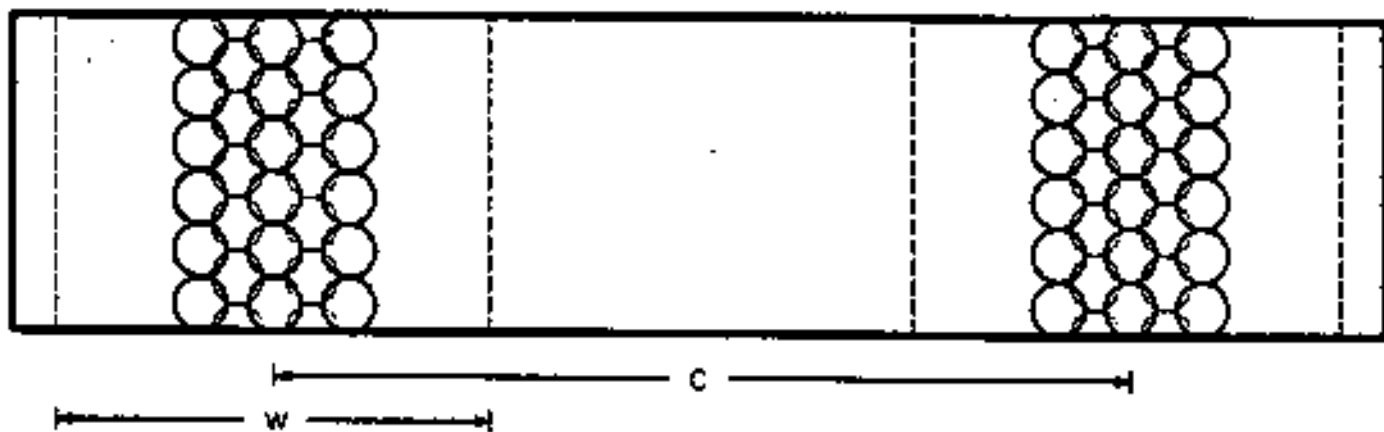
- We can apply a net drop in electric potential between neighboring slabs to induce net surface charges on the metal surfaces.

- Only the metal's valence electron wave functions are calculated; the H_2O molecules are taken to be closed-shell systems with fixed electron densities, as are the core electrons of the metal. We have done calculations for a model of copper in which only one electron per copper atom (an "s-like" electron) is treated explicitly and of cadmium in which two electrons per atom are treated explicitly. We emphasize mainly the results on the copper-like model here.

- The valence electron wave functions are taken to be zero outside of the "near–metal region"

- The wave functions are expanded in a basis of plane waves. Further details are quite standard and we refer to the papers.

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- For the copper like model, empirical pseudopotentials were used and only the s-like electrons of copper were included.

- For the cadmium model, full non-local pseudopotentials were used and no adjustment was necessary to get the cadmium work function right.

ATOMIC FORCES

After obtaining self consistent wave functions the atoms are moved with the Verlet algorithm using forces in the form

$$\vec{F}_i = \vec{F}_i^{atoms} + \vec{F}_i^{electrons}$$

- $\vec{F}_i^{atoms}$ were taken from water-water interactions from the central force model and electrostatic hydrogen-metal ion and oxygen metal ion interactions.

- $\vec{F}_i^{electrons}$ is the force on hydrogen, oxygen or metal atom i arising from the calculated valence electron density.

- $\vec{F}_i^{electrons}$ is obtained from $-\nabla_{\vec{R}_i} \int d\vec{r} \sum_{i,\nu} V_{ps}^{i,\nu}(\vec{r} - \vec{R}_{i,\nu})\rho(\vec{r})$ by Fourier transform of $V_{ps}^{i,\nu}(\vec{r} - \vec{R}_{i,\nu})$

# RESULTS FOR WATER DISTRIBUTION NEAR THE INTERFACE

- A calculation with just one water molecule in the space between the simulated copper slabs gave an on top site (oxygen down) as the lowest energy water configuration of the 100 structure.
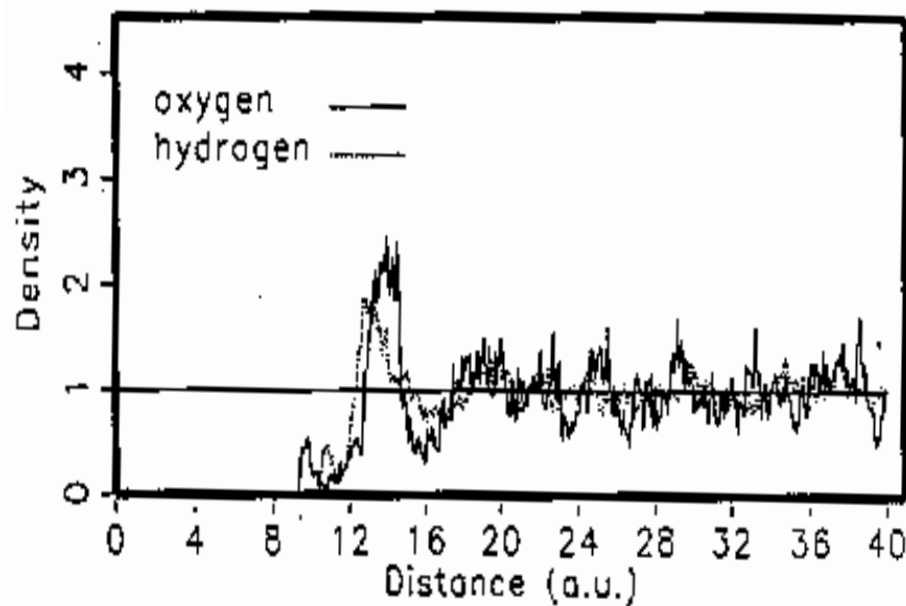
- Then we did a calculation with 245 molecules in the space between the planes and found the oxygen and hydrogen densities between the planes shown above.

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- It is evident that of all the "on-top" sites in the plane of the contour plot, only a few are occupied.

- This is very different from the results of the MD work of Heinzinger and Spohr, who would have made a potential using the one water molecule calculation and then found that nearly all the water molecules had attached in the on top site. Indeed, they did essentially this for a Pt surface. Evidently, the water is experiencing a "through metal" interaction in this model which causes one on-top water to repel another. This could not be represented by a two body potential.

Larry Curtiss and coworkers have confirmed that this "through metal" repulsion of water molecules on a copper surface occurs in a much more complete model of the electronic structure on a small cluster.
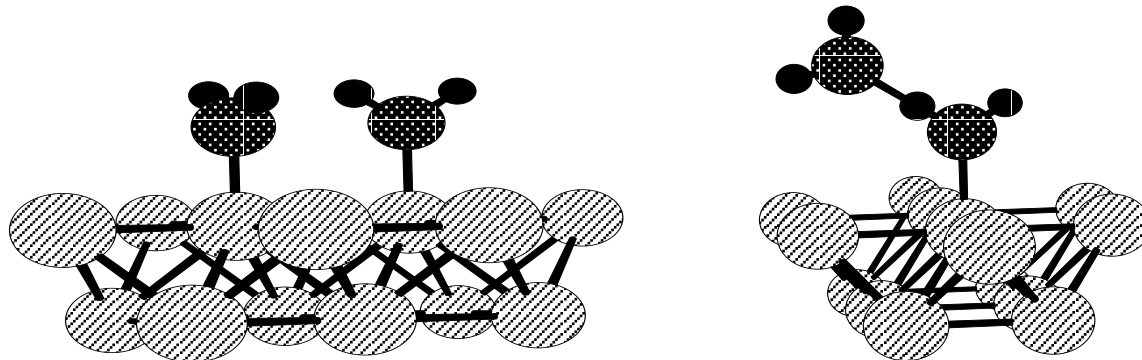
In the first configuration two neighboring waters are in on top sites. The binding energy of the second water molecule was only 0.03 eV, indicating a strong repulsion of a pair of near neighbors on top water molecules due to the "through metal" interaction. In the second configuration a second water was hydrogen bonded to the first water molecule, which was in turn in an on top site of the copper surface. The second water was bound by 0.38eV in the Hartree-Fock calculation.

CAPACITANCE: WATER-ELECTROLYTE SIDE
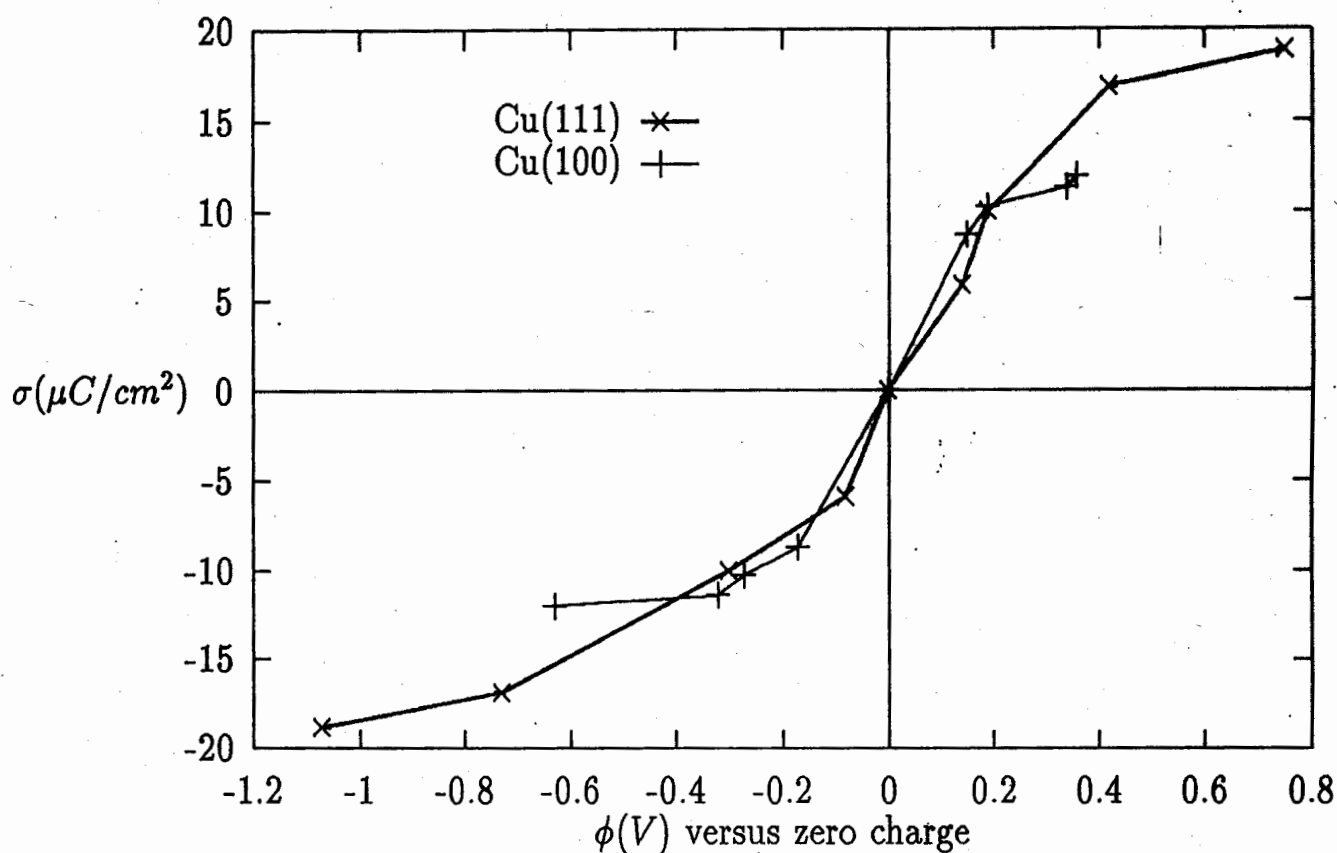
By imposing a field across the slab of the direct dynamics model of the metal water interface, we used the CP model to calculate the charge on the metal as a function of the total potential drop across the model interface as shown here. a) the 100 surface and b) the 111 surface of copper.

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The ions farther out in the solution eventually screen the field. It is NOT practical to include these directly in the simulation. At typical solution strengths there are about 100 water molecules per ion and we need around 100 ions to represent the double layer. The current Ewald methods scale as N^2 so the needed calculation would be approximately 10^8 times as expensive. (The simulation must be done many times for different field strengths.)

Furthermore, for dilute solutions and no specific adsorption, direct simulation of the ions is totally unnecessary, because the continuum Gouy Chapman model works very well.

The remaining problem is to correctly couple the continuum Gouy Chapman theory to the simulation of the "inner layer" metal and water parts of the simulation. We did this by calculation of the *macroscopic* electric field to provide a boundary condition for the continuum theory, as described next.

The boundary condition for the Gouy Chapman model can be estimated from the molecular dynamics simulation by calculating the macroscopic electric field at the plane $z = z_C$ at which the model begins to represent the system by the Gouy-Chapman model.

Given the macroscopic electric field $E(z)$ for a given charge σ on the electrode and assuming that in the continuum theory the solvent responds linearly to the field, we have, on the electrolyte side of z_C that

$$\frac{d}{dz}\epsilon(z)E(z) = 4\pi\rho(z)$$

where ρ is the ionic charge density in the electrolyte and we have allowed for the possibility that the local dielectric constant of the solvent is different from the bulk one, but have assumed a local response function.

We assume that all of the ionic charge is on the electrolyte side of z_C

The total ionic charge must exactly balance the charge σ on the electrode giving (since $E(\infty) = 0$)

$$-\epsilon(z_C)E(z_C) = -4\pi\sigma$$

If, as will usually be the case, the $E(z_C)$ so determined is not equal to $4\pi\sigma/\epsilon_{bulk}$ where ϵ_{bulk} is the bulk dielectric constant of the solvent , then we cannot simultaneously

1. use $E(z_C)$ as a boundary condition,

2. retain charge neutrality of the interface, and

3. use the Gouy Chapman theory in its usual form with a constant value of ϵ

Here we adopted a simple extension of the Gouy Chapman model in which ϵ varies smoothly with z from the simulation determined value $\epsilon(z_C) = 4\pi\sigma/E(z_C)$ to the bulk value far from the electrode:

$$\epsilon(z) = \epsilon(z_C) + (\epsilon_{bulk} - \epsilon(z_C))(1 - e^{\frac{-(z-z_C)}{z_o}})$$

Here $\epsilon(z_C) = 4\pi\sigma/E(z_C)$ is determined from the simulation by evaluating the macroscopic electric field at z_C.

The resulting model depended only weakly on the decay length, which was taken to be $z_O = 5\overset{\circ}{A}$.

With this form for $\epsilon(z)$ we numerically solved the Poisson-Boltzmann equation for $z > z_c$

$$-\frac{d}{dz}\epsilon(z)\frac{d\phi_{GC}}{dz} = 4\pi\rho(z) \qquad (1)$$

where ϕ_{GC} is the total electrostatic potential in the continuum model on the electrolyte side of z_c with the charge densi ty
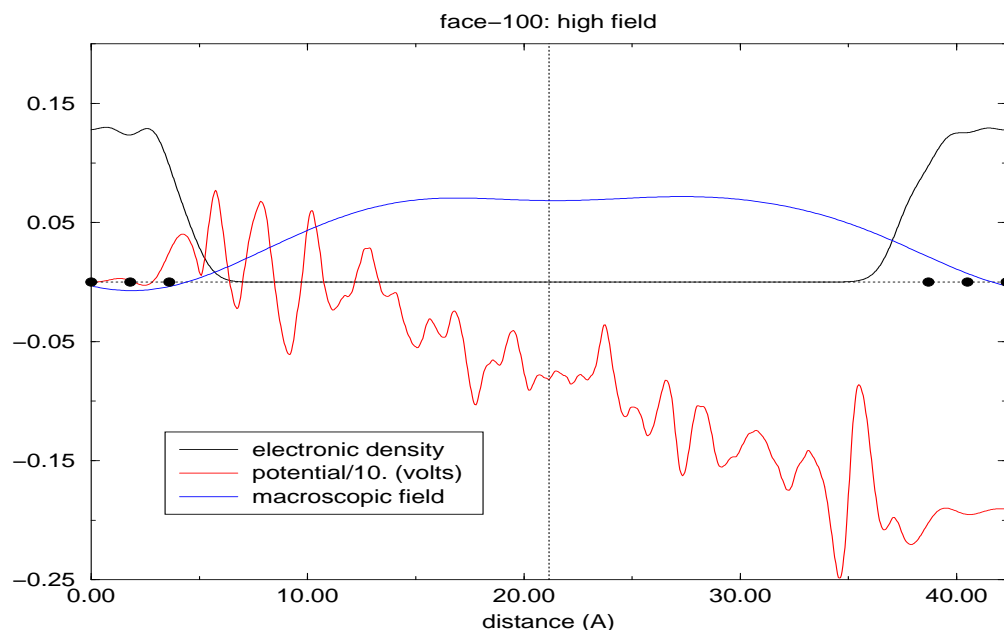
$$\rho(z) = 2n_oq_osinh(\beta q_o\phi_{GC}(z))$$

This yielded the net potential drop from inside the electrode to the bulk of the solution as

$$\phi = (\phi_{MD}(z \to -\infty)-\phi_{MD}(z = z_c))+(\phi_{GC}(z = z_c)-\phi_{GC}(z \to \infty)) \qquad (2)$$

$\phi_{MD}(z)$ is the electrostatic potential obtained from the simulation

$z \to -\infty$ is replaced by a point inside the model metal slab

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face−100: high field

electronic density
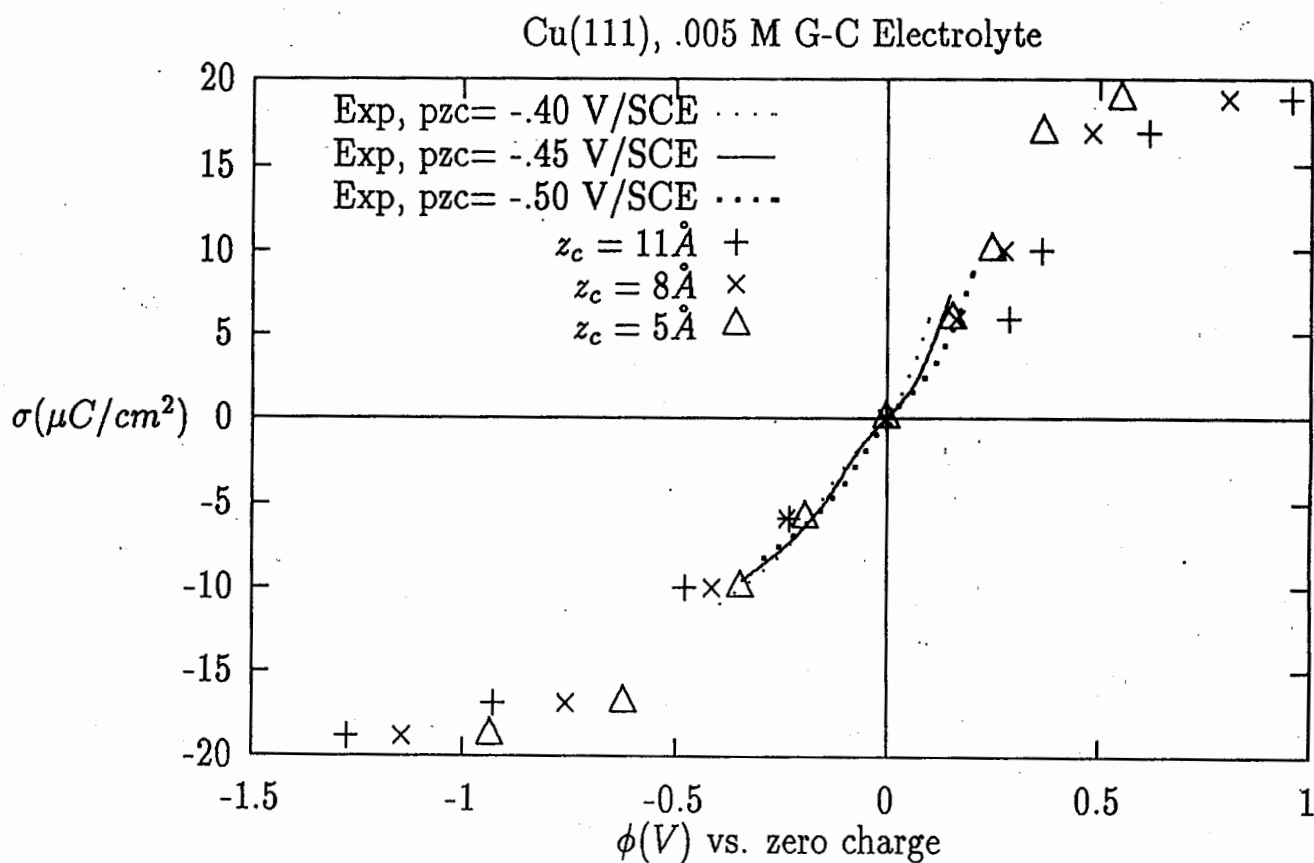potential/10. (volts)
macroscopic field

Values of the calculated macroscopic field for one field strength for the 100 face of copper.

The field near the interface is often calculated to be *lower* than in the bulk water, contrary to classical models.

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face−111: high field

macroscopic field	
potential/10. (volts)	
electronic density	
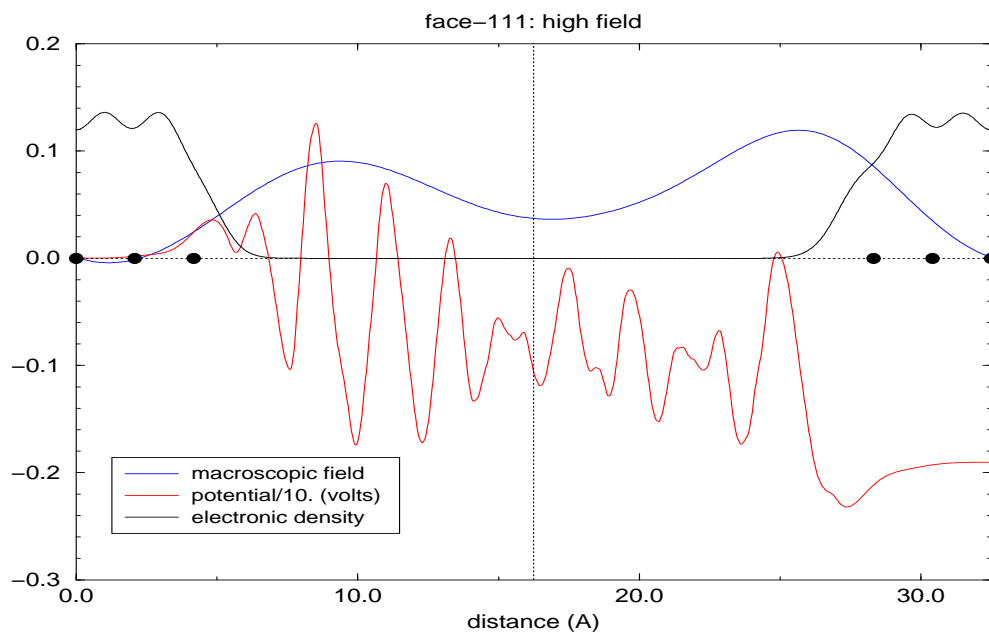
Values of the calculated macroscopic field for one field strength for the 111 face of copper.

Cu(111), .005 M G-C Electrolyte

Exp, pzc= -.40 V/SCE $\cdots$
Exp, pzc= -.45 V/SCE ——
Exp, pzc= -.50 V/SCE $\cdots$
$z_c = 11\text{Å}$ +
$z_c = 8\text{Å}$ ×
$z_c = 5\text{Å}$ △

Calculated and experimental differential capacitance for the 111 surface of copper. The reported potential of zero charge is -0.45 V/SCE for this surface.

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ELECTRON TRANSFER

- For *outer shell* electron transfer reactions, the problem is mainly a statistical mechanical one in the classical domain of calculating a free energy barrier height involving either solvent rearrangement or approach of the ion involved in the transfer to the electrode surface.

- We have studied to such reactions $Fe^{2+} \rightarrow Fe^{3+} + e$ at a gold electrode and $Cu^+ \rightarrow Cu^{2+} + e$ at a copper electrode in a collaborative program with Argonne National Laboratory.

How scales are coupled in the electron transfer problem;

- In reducing the problem to the calculation of a barrier height, one illustrates a way of coupling time scales accessible to molecular dynamics (up to nanoseconds) to reaction times which can be a million times slower. This works best when the reaction path can be definitively determined (and one path is dominant).

- With regard to length scales, in this problem we couple *ab initio* accessible scales (clusters) to molecular dynamics scales by fitting force field potentials to results of first principles electronic structure calculations (L. Curtiss). Two complications arose:

- The energies of multivalent ions surrounded by water turn out not to be representable by sums of two body force field potentials if the latter are derived directly from the first principles calculations on one ion interacting with one water molecule and pairs of water molecules.

- We need force fields for both reactant and product species in the reaction.

FORMAL TREATMENT OF THE ELECTRON TRANSFER PROBLEM

- Basic ideas are due to Rudy Marcus.

- In both homogeneous and heterogeneous electron transfer, the rate limiting step is the rearrangement of the atoms so that the intial and final electronic state are degenerate and electron transfer can occur.

- Marcus made classical electrodynamic models of the energy associated with the fluctuations in the free energy associated with the atomic motions which worked quite well over many systems and had appealing general features.

- These models lack microscopic predictive power.

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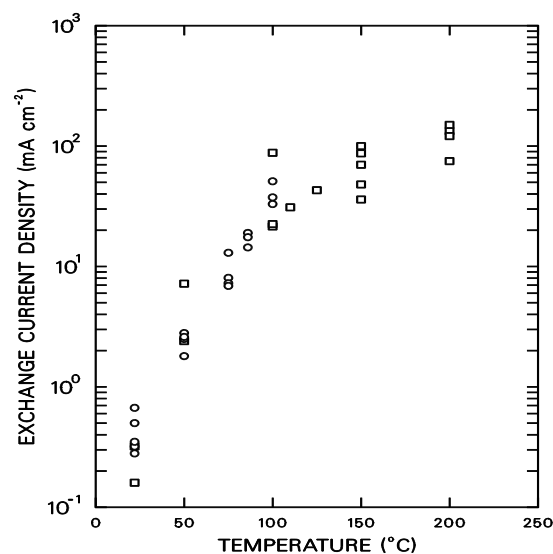
Measured exchange current density of the $Cu^{++} + e^- = Cu^+$ reaction. Circles: perchloric-acid–based solutions; squares: TFMSA–based solutions.

Arrhenius plot for the $Cu^{++} + e^- = Cu^+$ reaction. Circles: perchloric–acid–based solutions; squares: TFMSA–based solutions

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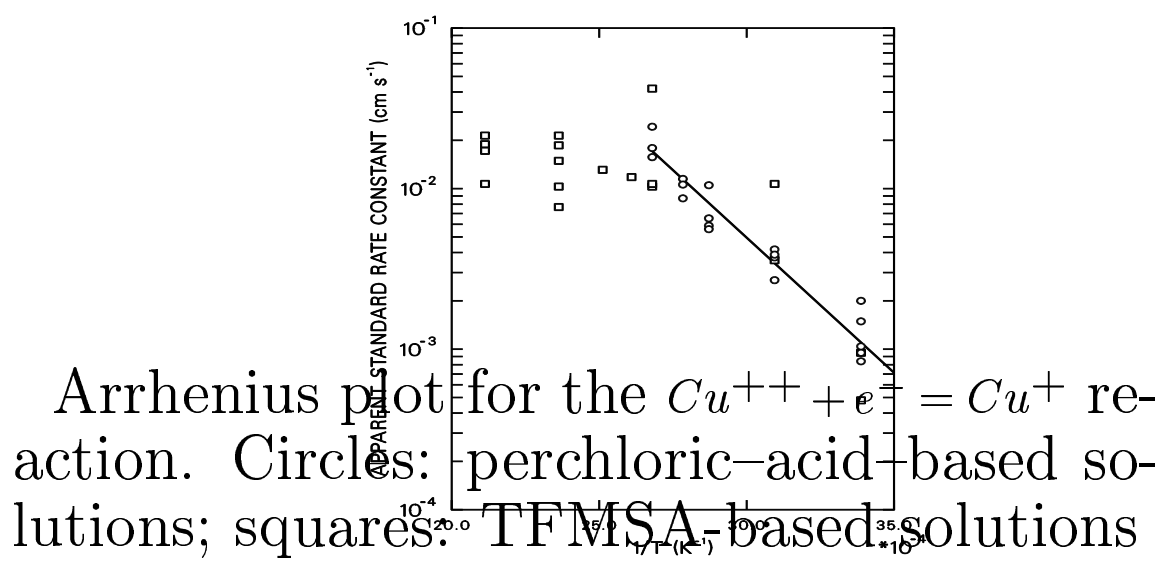
USE OF THE MODEL TO CALCULATE THE RATE

Diabatic Limit

$$rate = \frac{2\pi}{\hbar} <\mid \Lambda(\{R\}) \mid^2 \delta(V_i(\{R\}) - V_f(\{R\})) >_i \quad (3)$$

$$rate = \int dz \kappa(z) C_i(z) \quad (4)$$

$$\kappa(z) = \frac{2\pi}{\hbar} \mid \Lambda(z) \mid^2 < \delta(V_i(\{R\}) - V_f(\{R\}) >_{i,z} \quad (5)$$

$$C_i(z) = \frac{\int d\Omega e^{-\beta V_i}}{\int dR e^{-\beta V_i}} \tag{6}$$

$$\kappa_{ec} = \int dz \kappa(z) C_i'(z) \tag{7}$$

$$C_i'(z) = \lim_{L \to \infty} LC(z)$$

$$\kappa_{ec} = \frac{2\pi}{\hbar k_B T} \int dz \mid \Lambda(z) \mid^2 e^{-\beta F_{i,z}(\Delta E=0)} C'(z) \tag{8}$$

in which

$$F_{i,z}(\Delta E) = -k_B T \ln \left[\frac{k_B T \int d\Omega e^{-\beta V_i} \delta(\Delta E - V_i + V_f)}{\int d\Omega e^{-\beta V_i}} \right] \tag{9}$$

.

now write

$$C_i'(z) = \frac{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \delta(z - z')}{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \delta(z_{bulk} - z')} \equiv e^{-\beta F z(z)} \tag{10}$$

giving

$$\kappa_{ec} = \frac{2\pi}{\hbar k_B T} \int dz \mid \Lambda(z) \mid^2 e^{-\beta F_i(\Delta E=0,z)} \qquad (11)$$

$$F_i(\Delta E, z) \equiv \qquad F_{i,z}(\Delta E) \qquad + \qquad F_z(z) \qquad (12)$$

rearrangement approach

Calculation of Approach Activation Energy:

$$\frac{\partial F_z}{\partial z} = -k_B T \frac{\partial}{\partial z} \ln \left[\frac{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \delta(z-z')}{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \delta(z_{bulk} - z')} \right] = \tag{13}$$

$$-k_B T \frac{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \frac{\partial}{\partial z} \delta(z-z')}{\int d\Omega' e^{-\beta V_i(\{\Omega'\},z')}}$$

$$\frac{\partial F_z}{\partial z} = -k_B T \frac{\int d\Omega' dz' e^{-\beta V_i(\{\Omega'\},z')} \delta(z-z')(-\beta \frac{\partial V_i}{\partial z'})}{\int d\Omega' e^{-\beta V_i(\{\Omega'\},z')}} = < \frac{\partial V_i}{\partial z} >_{i,z} \tag{14}$$

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Calculation of Rearrangement Activation Energy

$$F_{i,z}(\Delta E) = -k_B T \ln \left[\frac{k_B T \int d\Omega e^{-\beta V_i} \delta(\Delta E - V_i + V_f)}{\int d\Omega e^{-\beta V_i}} \right]$$

$$(15)$$

.

Adiabatic Limit

$$V = \begin{pmatrix} V_i & \Lambda \\ \Lambda & V_f \end{pmatrix}. \tag{16}$$

$$F_{-,z}(\Delta E) = -k_B T \ln k_B T < \delta(\Delta E - V_- + V_+) >_{-,z} \tag{17}$$

$$\Delta E' = V_- - V_+ - 2\Lambda(z)$$

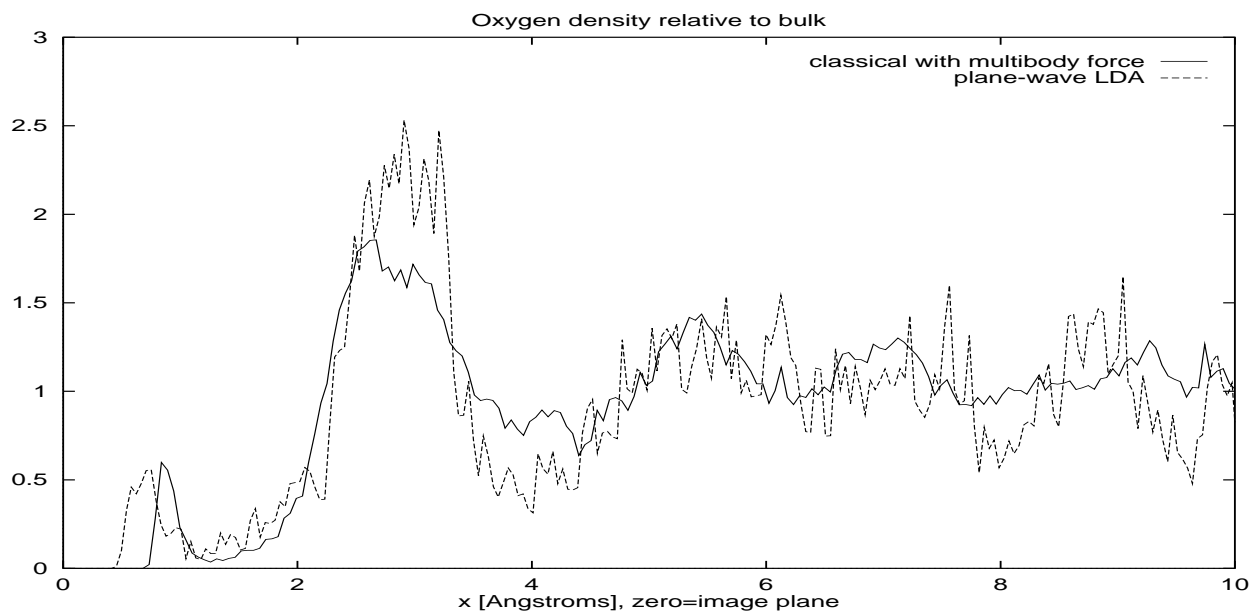Umbrella sampling techniques are discussed in the references.

MOLECULAR DYNAMICS MODEL

- Central force model for the water (K. Toukan and A. Rahman, Phys. Rev. B31, 2643 (1985))

For copper, we fit some characteristics of an almost ab initio density functional theory model of the copper water interface (S.Walbran, J. W. Halley, A. Mazzolo and D. L. Price J. Chem. Phys. and J. Chem. Phys. 102, 6603 (1995)), described above. We took partial account of the "through metal" interaction by use of a classical three-body potential

$$U(\vec{r}_1, \vec{r}_2) = Ce^{-r_\perp^2/(r_o/2)^2} \left(e^{-z_1/z_0} + e^{-z_2/z_0} \right) \quad (18)$$

We used $C = .001e^2/\mathring{A}$, $r_0 = 10.0\mathring{A}$, $z_0 = 1.0\mathring{A}$.

Oxygen density relative to bulk

classical with multibody force ———
plane-wave LDA - - - - -

x [Angstroms], zero=image plane

Density of oxygen as a function of distance z from the electrode in the model, compared with results from the better, CP model described above.

Short range Cu+1 and Cu+2 potentials
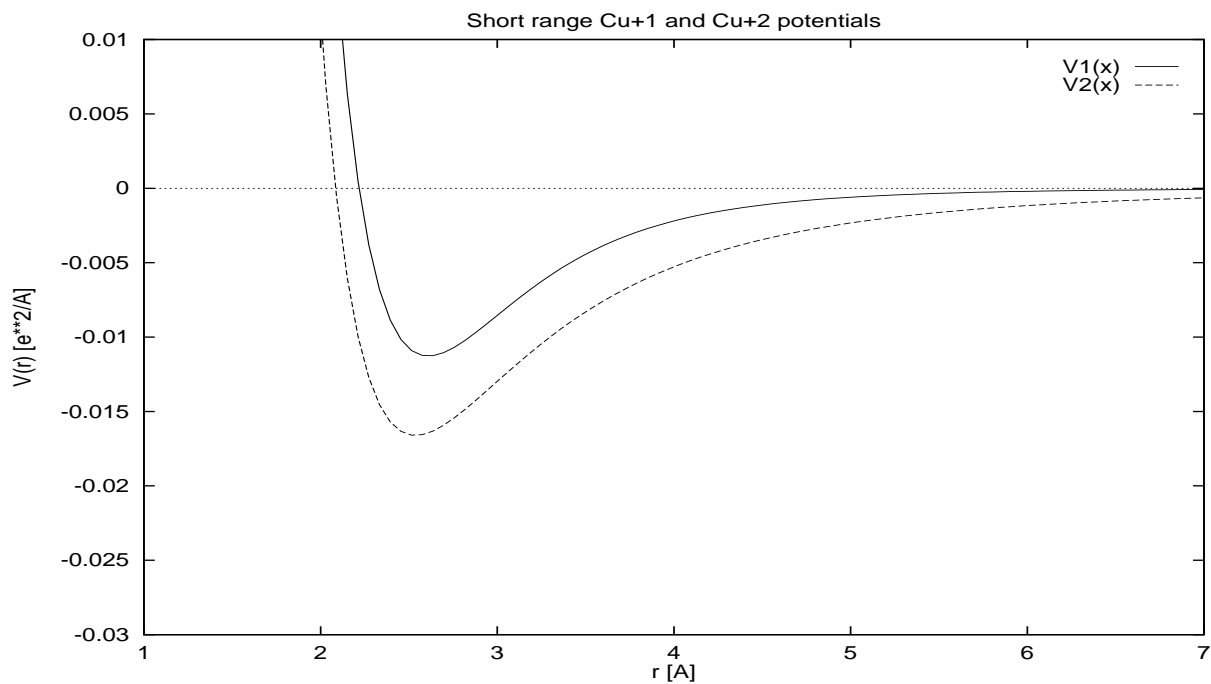
Copper-oxygen pair potentials (in $e^2/\overset{\circ}{A}$) used in simulation as a function of radial separation r in $\overset{\circ}{A}$. From Hartree-Fock (quantum chemical) calculations by L. Curtiss. The coulomb interaction $q_{Cu}q_O/r$ is not included.

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Solvation Energies of the Ions. These had to be right to get quantiative results for electron transfer energy barriers.:

		Simulation (kJ/mol)	Experiment (kJ/mol)
$E_{solvation}$,	Cu^{+1}	580 ± 70	576
$E_{solvation}$,	Cu^{+2}	2085 ± 70	2105
ΔE		1505 ± 70	1529
ΔF		1485 ± 70	1481

EQUILIBRIUM POTENTIAL

The equilibrium is achieved when the concentrations of the Cu^{+1}, Cu^{+2} are given by

$$\frac{[Cu^{+2}]}{[Cu^{+1}]} = e^{-\beta \Delta F} \tag{19}$$

The components of the free energy difference ΔF are

$$\Delta F = I - \Delta F_{solv} - \Delta \phi^{\sigma}_{H_2O} - \Phi$$

Approximate values:

Contributions to the free energy difference.

| Symbol	Meaning	Source	Typ. Value
I	Ionization energy	Exp	20.3 eV
ΔF_{solv}	Solvation difference	Sim	15.4 eV
$\Delta\phi^{\sigma}_{H_2O}$	Electro-static drop	Sim	0.3 eV
Φ	Work function	Exp	4.6 eV

Calculation within the MD model with inclusion of buffering electrolyte (treated in GC theory) gives:

Equilibrium potential minus PZC =0.25 V (MD model)

Equilibrium potential minus PZC = 0.5-0.8 V (Experiment)

Here we were coupling the MD to the CONTINUUM Gouy Chapman model, using methods like those discussed above when we discussed capacitance.

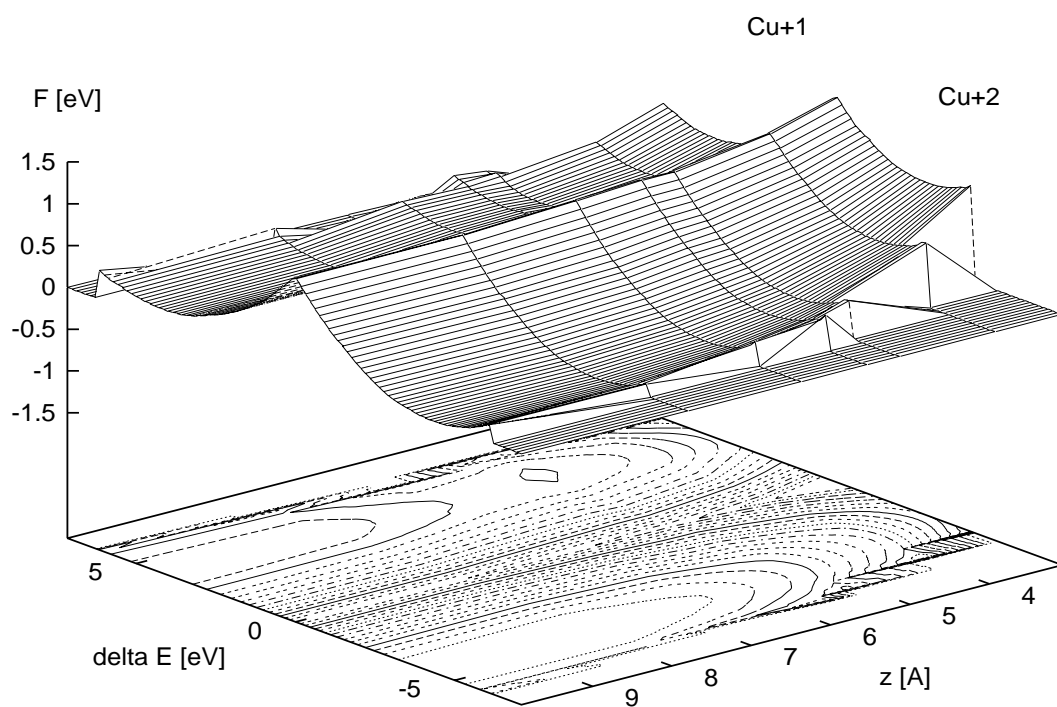# ONE MORE INPUT FROM MICROSCOPIC CALCULATON: THE COUPLING CONSTANT
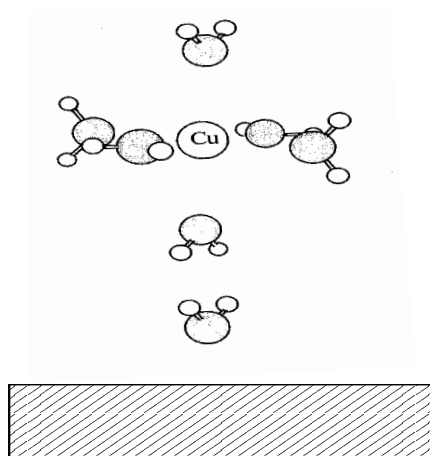
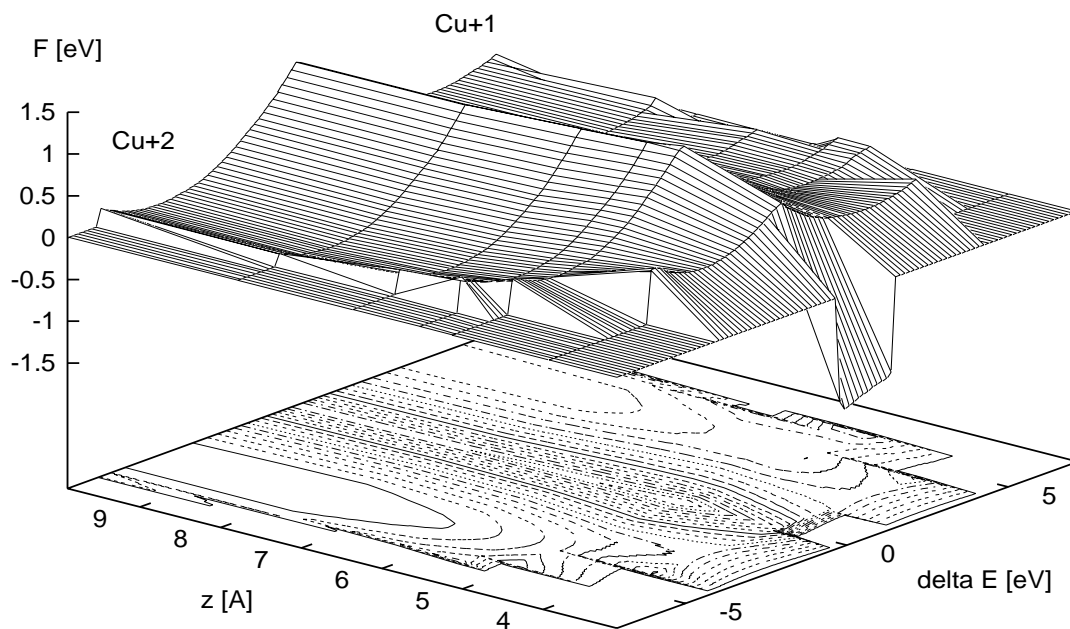The "apex" approach of the hydrated copper ion to the copper surface used to calculate the electronic matrix element.
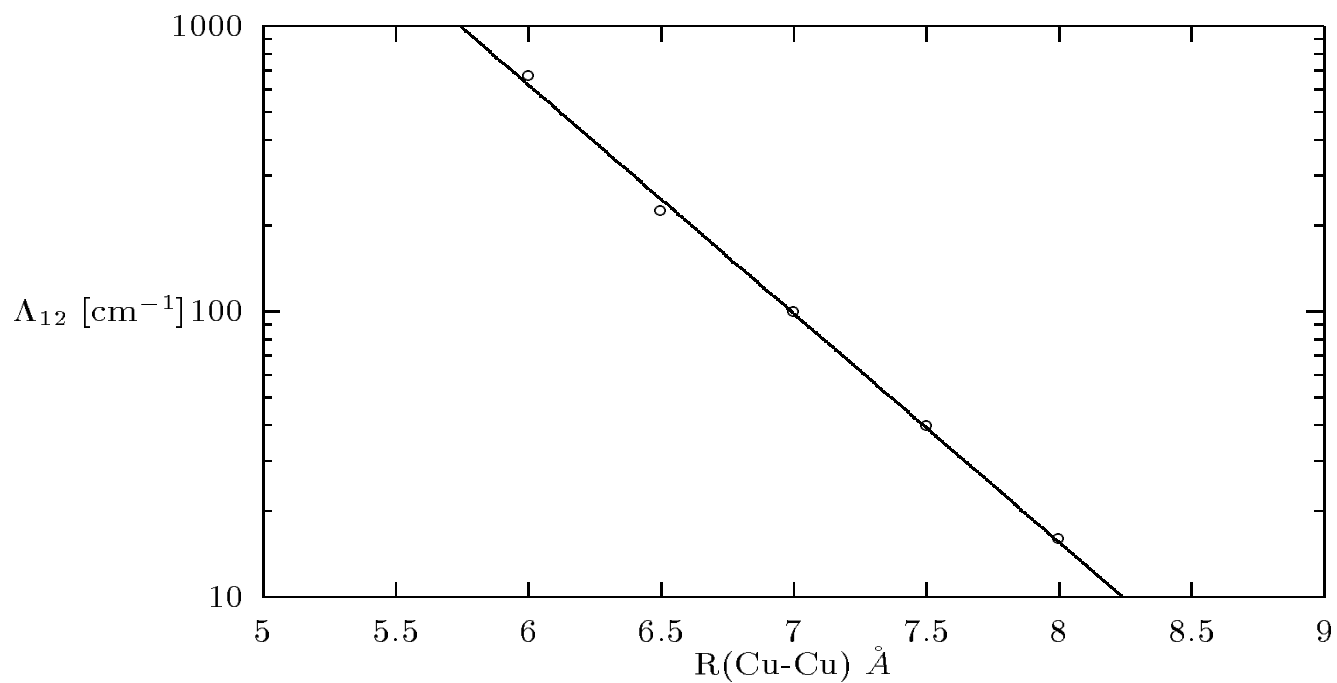
Λ_{12} as a function of distance of the copper ion from the copper surface.

Diabatic Free Energy Surfaces for the Cuprous and Cupric Ions.

Adiabatic Free Energy Surfaces for the Cuprous and Cupric Ions

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Results for the kinetic barrier for the cuprous-cupric electron transfer reaction.

Theory	Values	
	(eV $\pm$ 0.1 eV)	(kJ/mol$\pm$ 10 kJ/mol)
Diabatic	1.30	125
Adiabatic, ,1st Λ	0.43	41
Adiabatic, , 2nd Λ	0.17	16
Experiment		32$\pm$ 5

TRANSFER COEFFICIENT

Calculational Estimates of the Transfer Coefficient

σ $(\mu C/cm^2)$	F_{act} (eV)	δF_{act} (eV)	$\delta\Phi$ (eV)	β
0.	0.37	0.06	0.25	0.24
5.	0.43			
9.	0.58	0.15	0.81	0.19

Experimental β $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 0.59±0.5
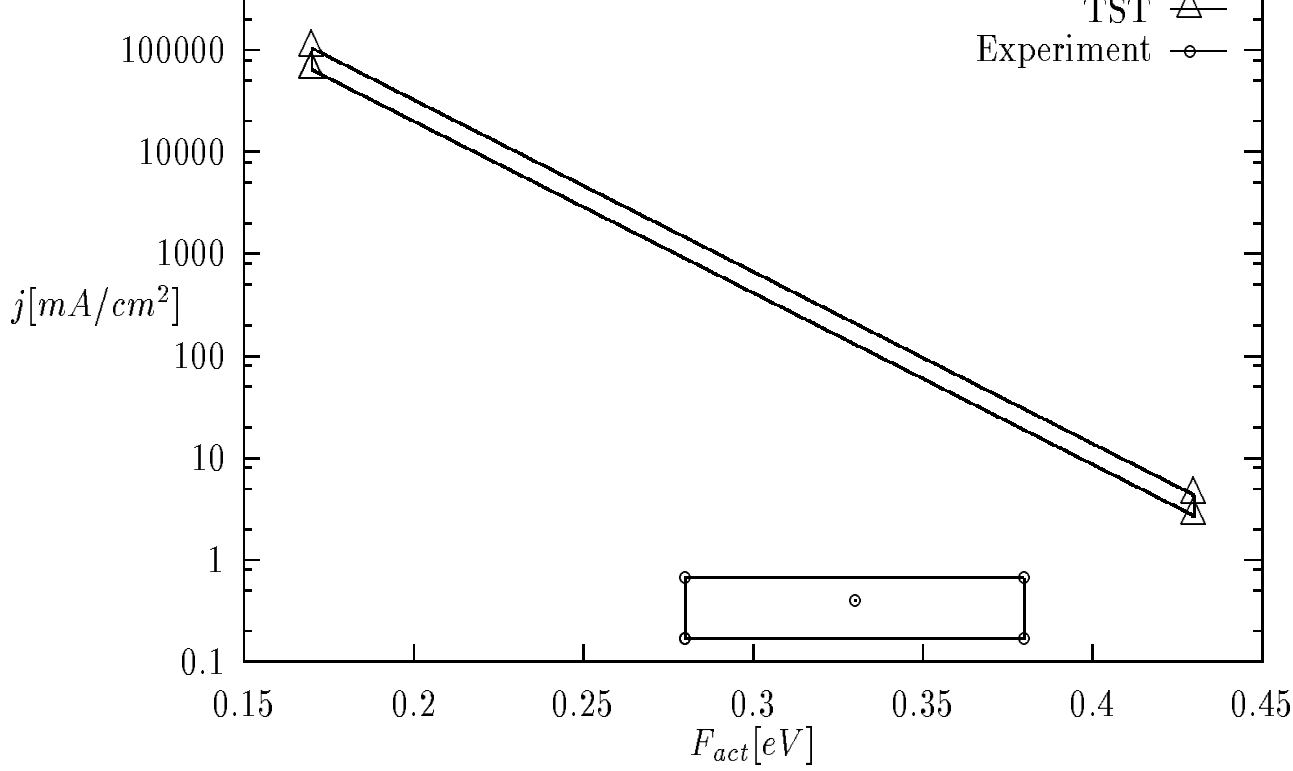
Comparison of experimental exchange currents with transition state theory as a function of activation energy. The vertical sides of the upper box correspond to the two values of activation energy calculated (independent of transition state theory) in the model with two choices for the function $\Lambda_{12}(z)$. The top and bottom sides of this upper box correspond to two choices of m_r in TST . The lower box shows the range to which the experimental current and activation energy are confined.

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CONCLUSIONS

- Models of these interfaces require quantitative detail at all scales from tenths of angstroms (electronic structure) through angstroms (atomic structure, MD) through continuum behavior at 10's of nanometers and beyond.

- They provide a great testing bed for scale matching in simulation.